

SYNTHESIS AND APPLICATION OF SILICA GEL BASE ON MOUNT SINABUNG'S FLY ASH FOR Cd(II) REMOVAL WITH FIXED BED COLUMN

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ABSTRACT

Synthesis of silica gel base on Mount Sinabung's volcanic ash taken from different villages, was carried out. The purposes of this research are to synthesis and characterized by silica gel which was generated base on ash. The method of this research is a sol-gel method. The silica gel was characterized by Fourier Transform Infra Red (FTIR), X-Ray Diffraction (XRD), and Barret Emmet Teller (BET) respectively. The silica gel consists of Si-O-Si and Si-OH groups. XRD data also shows that silica is amorphous. BET data show that the surface area of silica gel is 374.994 m²/g. A fix bed Column of silica gel was used for the removal of Cd(II). The adsorption column used has a diameter of 1.7cm and is filled with 0.5g of silica. the optimum adsorption capacity is: flow rate 4mL / min (21,194 mg / g). The initial optimum concentration is 24 ppm (21.632 mg / g). The optimum pH is pH 6, (21.848 mg / g). The experiment result showed silica adsorbent effective for removal Cadmium

Keywords: Silica volcanic ash of Sinabung, adsorption, cadmium, fixed bed column.

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INTRODUCTION

Sinabung's mountain is one of the active volcanoes which is located in North Sumatra province-Indonesia. Its coordinates are 03°10' LU dan 98° 23' BT with the highest peak of 2,460 meters above sea level. This mountain is very interesting due to it has erupted since 2010 until now ¹. It is constantly erupting and expelling millions of cubic volcanic ash materials. The abundance of mountain volcanic ash material as a result of the eruption of Mount Sinabung is an interesting thing to be studied and utilized further.

Several studies have shown that volcanic ash volcanoes contain mainly silica material². Zuarida reported that amount silica oxide (SiO₂) on Kelud volcanic mountain's ash is 45.9%³, Merapi volcanic mountain's ash is 56.39%⁴, Sinabung volcanic mountain's ash is 58,10%⁵ and 74.3%⁶. It means the ash is Sinabung mountain's higher than others and very potential as a raw material to produce adsorbent base on silica.

Silica is a giant molecule and usage as an adsorbent. It is possible because its large pore and have both silanol group (-Si-OH) and siloksan (-Si-O-Si-) as an active site. There are four oxygen atoms on Si; it may be used as an active site to bind metal namely chemical bonding between Si-Metal⁷.

The fast growth of the various industry caused increase waste and contributes the pollution of aquatic environment^{8,9}. Heavy metals are known to have high toxicity and carcinogenic which tends to affect the lives of humans and other living beings. This is because heavy metals are very difficult and furthermore they are resistant to bacteria or decomposition processes which result in excessive accumulation of concentrations in the aquatic environment exposed by heavy metals continuously¹⁰⁻¹⁴. Cadmium is one of the most toxic and harmful metals. This is dangerous for humans because in relatively small quantities can lead to death in poisoned creatures. This is due to the biological systems of the human body, these metal are non-essential. Industrial activities involving cadmium use include textile industry, battery manufacture, metal coating, paint / color ink, printing, agrochemicals etc.¹²⁻¹⁴

Most about studies adsorption process of heavy metals using adsorbents as rice husk ash^{12,19-21}, fly ash^{13,17-18}, coal fly ash¹⁵⁻¹⁶, peat and mollusk¹⁴, activated carbon¹⁰, moringa oleifera bark¹¹ have been done. The adsorption process about used of adsorbents such as rice husk ash, fly ash, peat and mollusk shell, chitin²², algae²³ have been widely used in the release of Cadmium in both wastewater and aqueous solution using fixed bed column studied is report¹²⁻¹⁴. But the use of volcanic ash as an adsorbent to removal Cadmium has not been used. There are only a few studies that have used volcanic ash as an adsorbent²⁴⁻²⁵. Base on recent situation the main objective of this research was to determine the adsorption capacity of silica gel from volcanic ash Sinabung as an adsorbent to removal cadmium from aqueous solution by fixed bed column method including flow rate, pH, and concentration of Cadmium.

EXPERIMENTAL

The volcanic ash was taken from four villages at Kecamatan Simpang Empat- Karo District, those are Desa Beras Tepu, Sigarang-garang, Kuta Gunggung, and Kuta Rakyat. The villages distance is around 3, 4, 5 and 6 Km to the top side of Sinabung Mountain. Then, it was brought to research laboratory of Chemistry Department- University of State-Medan. Subsequently, it calls as a sample.

Characterization of Volcanic Ash

The sample was sieved to generate the homogenized sample (200 mesh). After that, the sample was characterized with XRF.

Synthesis of Silica

20 gram of volcanic ash was soaked into 120 mL HNO₃ for 24 hours. Then, it was dried on the oven at T = 120° C and 6 hours and its weight were recorded. Subsequently, the volcanic ash was destructed with 156 mL NaOH 4M until the viscous at the furnace. It will be carried out at 500 °C and 30 minutes. After that, it was added 200 mL water for 24 hours. Finally, the solution was filtered and characterized by using AAS. It is denoted as Na-Silicat (Na₂SiO₃)

Synthesis of Silica Gel

20 mL Na-Silica solution was put into porcelain. HCl 3M was gradually dropped on Na-Silica and stirred until the white gel was formed and pH gel was neutral. Then, silica gel was filtered and rinsed with water until its pH was neutral. Finally, silica gel was dried into the oven under conditions T = 120 °C for 6 hours. Silica gel was characterized by using AAS, FTIR, XRD and Surface Area Analyzer, respectively.

Fixed Column Adsorption Studies of Cd(II)

Silica gel that had synthesized used as adsorbent using fixed column method. The column that was used has the diameter of 1.7cm and the amount of silica used in each study was 0.5 grams. The respective concentration of Cd(II) solution flowed through the column with the respective amount flow rate and pH value. The effluent solution then collected every 15 minutes and the concentration was measured to calculate the adsorption capacity of each study to determine the optimal amount of flow rate, initial concentration, and pH value of column adsorption.

RESULTS AND DISCUSSION

Formation of Silica Gel

The gray smooth powder of volcanic ash was characterized by XRF analysis to examine the main components of Sinabung volcanic ash. The result shows Si content is 91.4% , then was converted as SiO₂ content of volcanic ash is 42.65%²⁶. It indicates the volcanic ash has a cement pozzolant material with high SiO₂ concentrate. Formation of silica gel is started by reacting between volcanic ash and NaOH 4M at T = 500 °C. Sodium hydroxide is dissociated at that temperature to form sodium and hydroxide ions. At SiO₂, electro negativity of oxygen is higher than silica (Si), so Si is much more electropositive and forms intermediate [SiO₂OH]⁻ which it is unstable and dehydrogenation occur. Ion Na⁺ will react with SiO₃²⁻ to form sodium silica (Na₂SiO₃).The mechanism reaction is shown in Fig.-1²⁷.

Table-1: Composition of Sinabung Mountain's Volcanic Ash

Volcanic ash components	Amount(%)
Si	91.4 ± 0.1
K	3.09 ± 0.02
Ca	2.60 ± 0.02
Cr	0.086 ± 0.003
Mn	0.19 ± 0.03
Fe	0.54 ± 0.01
Ni	1.09 ± 0.02
Cu	0.18 ± 0.003
Zn	0.32 ± 0.01
Ga	0.090 ± 0.003
Eu	0.2 ± 0.02
Re	0.3 ± 0.03

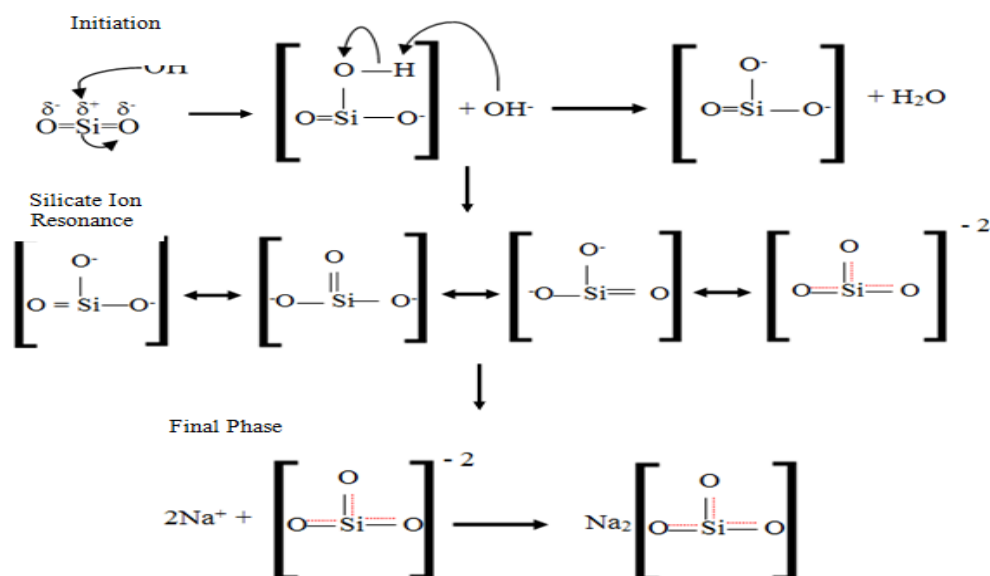


Fig.-1: Mechanism reaction of Sodium Silicate formation

Silica gel was formed by using sol-gel preparation method using hydrochloric acid. When, hydrochloric acid was added, it caused ionic exchange between H⁺ and Na⁺ to form silicic acid which did not dissolve in the solution.²⁸ The formation of silica precipitates was observed at pH

14, however, the gel precipitates started to form at pH 8 to 10. And the addition of hydrochloric acid was stopped at pH 7. In the formation of silica gel, the silicic acid which formed from the reaction between hydrochloric acid and sodium silicate solution exhibited water polycondensation to form dimers, trimers, and polymers of silicic acid thus releasing water molecule in the process.²⁹

Silicic Acid Formation

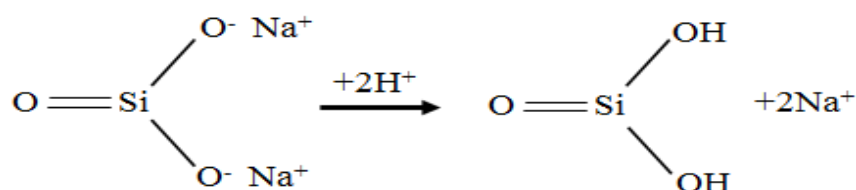


Fig.-2: Mechanism Reaction of Silicic Acid Formation

FTIR Analysis

Silica gel also was characterized by using FTIR. FTIR data is shown in Fig.- 4. The broad peak of 3433.29 cm^{-1} is a specific peak for hydroxyl functional group ($-\text{OH}$). Normally, $-\text{OH}$ group should appear at 3500 cm^{-1} . It means there is an interaction between electropositive substances and $-\text{OH}$, namely $\text{Si}-\text{OH}$ (2862.36 and 2927.94 cm^{-1}). Therefore, the peak shifts to the lower wave length number. Thereby, the type silica of volcanic ash is probably $\text{Si}-\text{OH}$ or $\text{Si}-\text{O}-\text{Si}$. In addition, the sharp and broad peak at 1095.57 cm^{-1} also indicates $\text{Si}-\text{O}-\text{Si}$ is there. That is also supported by appearing peak at 466.77 cm^{-1} , 798.53 cm^{-1} and 2357.01 cm^{-1} as well as $\text{Si}-\text{O}-\text{Si}$

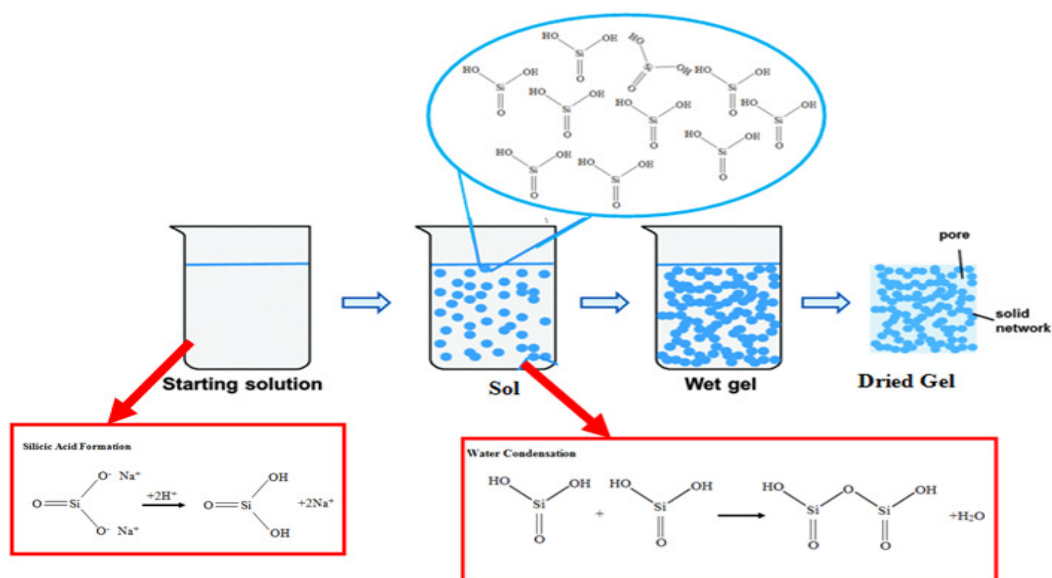


Fig.-3: Mechanism of Sol-Gel Reaction

XRD Studies

XRD curve for the prepared of Silica gel from different villages with sol-gel methods is showing in Fig.-5.

XRD patterns show broad peaks at $2\theta = 20-24^\circ$. It indicates silica that the XRD data of volcanic ash from Kuta Rakyat, Kuta Gunggung, Sigarang-Garang, Beras Tepu is shown the 2θ number of Beras Tepu is lowest among the others ($2\theta = 21.8800$) with a diameter (d) = 4.05889 Å (0.4059 nm). On the other hand, 2θ number of Kuta Rakyat is highest among the others $2\theta = 24.2600$ with $d = 3.66582$ Å (0.3665 nm). XRD data also shows that the silica is amorphous which it is possible to be applied as adsorbent²⁹.

Analysis of BET

Characterization of silica surface area is characterized by BET aims to determine the pore radius and surface area of silica gel. Base on XRD data, silica gel of Beras Tepu is so special due to crystal and the 2θ number. Therefore, the BET number is determined. Figure-6 presents the nitrogen adsorption/desorption isotherms measured for the silica.

The results showed that the average pore radius of $1,5469 \times 10^{-1}$ Å, pore volume total of $2,900 \times 10^{-1}$ ml/g for pores smaller than 1387.4 Å (Radius), surface area 374,994 m²/g. Base on The International Union of Pure and Applied Chemistry (IUPAC) that the silica gel is micropore³⁰. Compared with previous research, the synthesis of silica gel from sands of southern Tunisia, which is specific surface area exceeded 340 m²/g³¹ is much wider, so it is suitable for use as an adsorbent in the adsorption process.

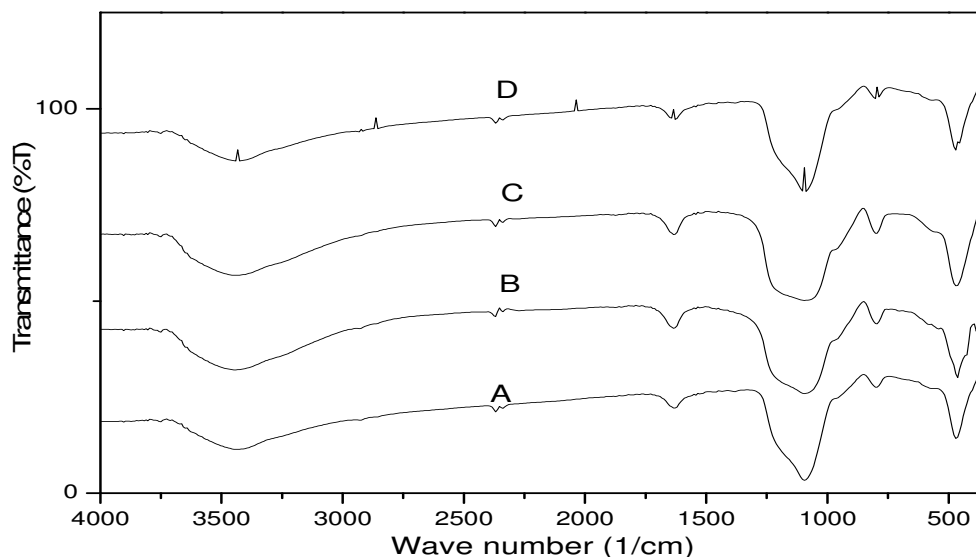


Fig.-4: FTIR Spektra of Silica from A.Kuta Rakyat, B. Kuta gunggung, C. Sigarang-garang, D. Beras Tepu

Fixed Column Adsorption Studies of Cd(II)

Effect of Influent Flow Rate

An adsorption study was carried to determine the optimal flow rate of Cd(II) adsorbate in the column adsorption. The flow rates variations were 3mL/min, 4mL/min, and 5mL/min. The adsorbate concentration used was 24 mg/L and the pH of influent was adjusted to 5. The experimental parameter is described in Table-2. In order to determine the optimal influent flow rate, the breakthrough point and the adsorption capacity of each column study are calculated. The breakthrough point of each column study is shown in Fig.-7.

The result shows that the adsorption capacity of Cd(II) is increasing flow rate 3mL/min to flow rate 4mL/min then decreases in flow rate 5mL/min. An increase in flow rate reduces the metal ion solution treated efficiently until a breakthrough point and therefore decrease the contact time between the metal ion and the silica gel. When the flow rate decreases, the contact time in the column is longer, pore diffusion then becomes effective. Thus metal ions have more time to diffuse to the porous of silica column and the better adsorption capacity is obtained³². However, the

increasing adsorption capacity from flow rate 3mL/min to 4mL/min is happened due to the optimal effect of silica gel, where from experiment the optimal adsorption capacity obtained is at flow rate 4mL/min.

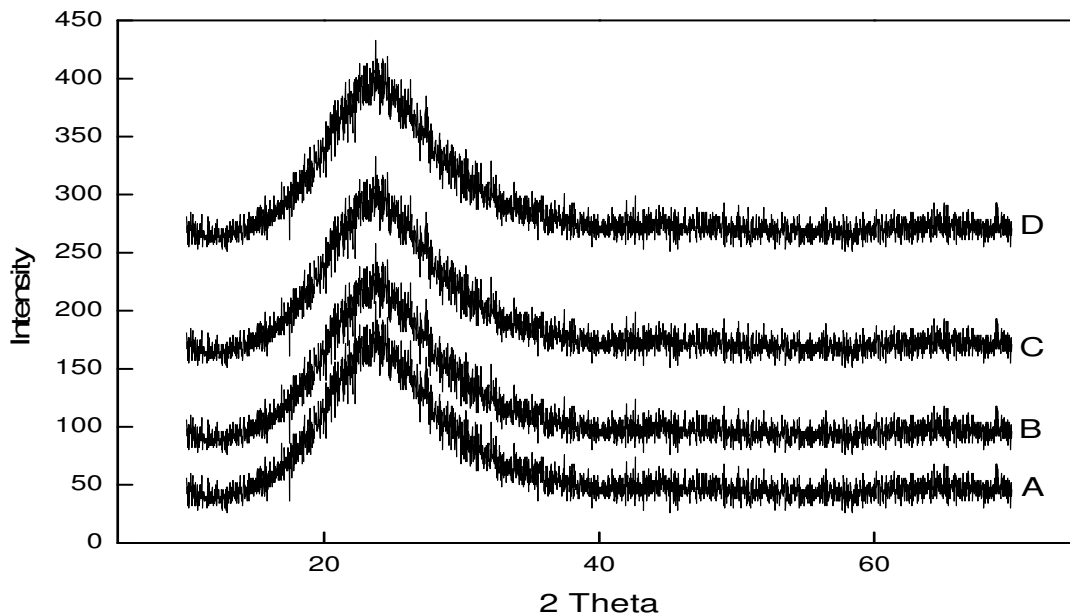


Fig.- 5: XRD image of Silica from A.Kuta Rakyat, B. Kuta gunggung, C. Sigarang-garang, D. Beras Tepu

Table-2. The experimental Parameter of Adsorption Study Using Different Flow Rate

Experimental parameters	Fixed Bed Column Adsorption Experimental		
	Experiment 1	Experiment 2	Experiment 3
Influent Flow Rate (mL/min)	3.00	4.00	5.00
Influent Cadmium Concentration (mg/L)	24.00	24.00	24.00
Silica Gel (g)	0.50	0.50	0.50
pH of Influent Solution	5.00	5.00	5.00
Service Time (min)	180	180	180
Total Cadmium Solution Treated (L)	0.54	0.72	0.90
Total Cadmium Adsorbed (mg)	9.879	10.690	9.806
Adsorption Capacity (mg/g)	19.759	21.380	19.612

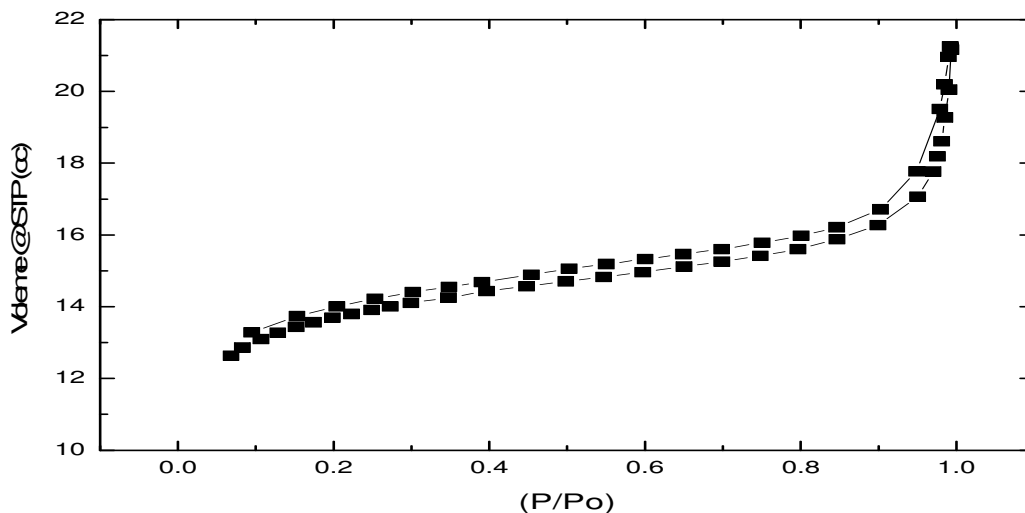


Fig.- 6: Isotherms Data Measured at 77.350K

Table-3: Experimental Parameter of Adsorption Study Using Different Initial Concentration

Experimental parameters	Fixed Bed Column Adsorption Experimental		
	Experiment 1	Experiment 2	Experiment 3
Influent Flow Rate (mL/min)	4.00	4.00	4.00
Influent Cadmium Concentration (mg/L)	20.00	24.00	30.00
Silica Gel (g)	0.50	0.50	0.50
pH of Influent Solution	5.00	5.00	5.00
Service Time (min)	180	180	180
Total Cadmium Solution Treated (L)	0.72	0.72	0.72
Total Cadmium Adsorbed (mg)	10.116	10.815	9.718
Adsorption Capacity (mg/g)	20.232	21.631	19.437

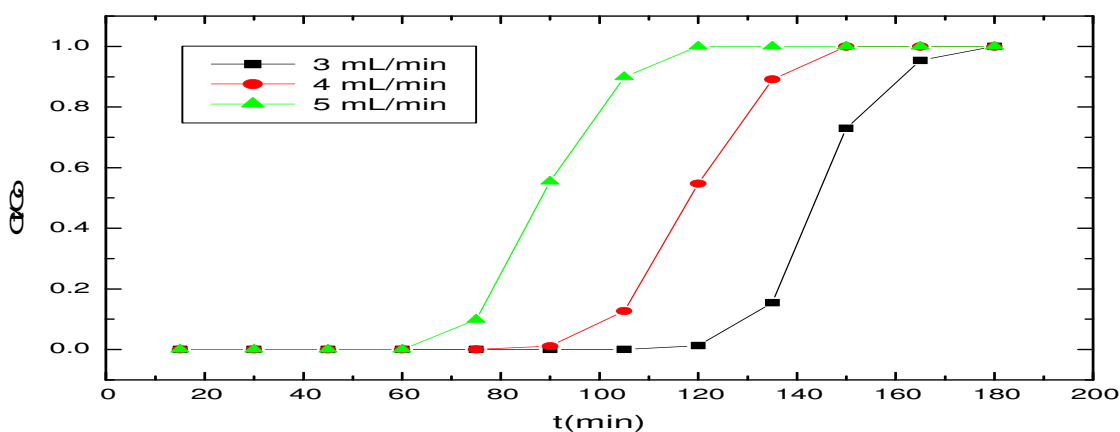


Fig.-7: Breakthrough Curves for Cadmium(II) Adsorption by Silica for a Different Flow Rate of, 3, 4 and 5 mL/min

Effect of Initial Influent Concentration

The optimal flow rate of 4mL/min which obtained from the first study was used in this study. Where the initial concentrations used were 20 mg/L, 24 mg/L, and 30 mg/L. The pH of influent was adjusted to 5. The experimental parameter is described in table 3 and The breakthrough point of each column study is shown in Fig.-8.

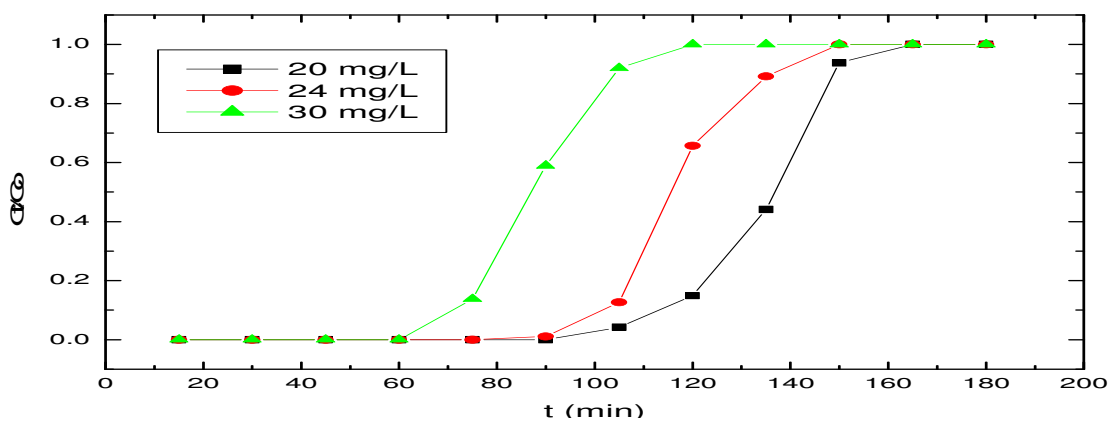


Fig.-8: Breakthrough Curves of Cd(II) Removal by Silica for the Different Initial Concentration of 20, 24 and 30mg/L

The result shows that the highest adsorption capacity is at initial influent concentration 24mg/L. The amount of initial influent concentration effects the adsorption capacity of metal ion, where the increasing of initial concentration causing the saturation of adsorbent porous more quickly. When the saturation has occurred on the adsorbent layer, the further contact with metal ion would cause

two conditions. The first condition is the formation of another layer, thus creating the multilayer adsorption. And the other condition where the adsorbed metal ion escapes from adsorbent porous and diffuses back to the solution. The adsorption of Cd(II) ions by silica gel follows the second condition, where the increasing initial influent concentration which higher than the optimal concentration will cause a drop in adsorption capacity.

Table-4: Experimental Parameter of Adsorption Study using Different pH

Experimental parameters	Fixed Bed Column Adsorption Experimental		
	Experiment 1	Experiment 2	Experiment 3
Influent Flow Rate (mL/min)	4.00	4.00	4.00
Influent Cadmium Concentration (mg/L)	24.00	24.00	24.00
Silica Gel (g)	0.50	0.50	0.50
pH of Influent Solution	5.00	6.00	7.00
Service Time (min)	180	180	180
Total Cadmium Solution Treated (L)	0.72	0.72	0.72
Total Cadmium Adsorbed (mg)	10.840	10.924	10.478
Adsorption Capacity (mg/g)	21.681	21.848	20.957

Effect of Influent pH Value

These studies were carried out to determine the optimal pH value of Cd(II) ions adsorption. Where the optimal flow rate of 4mL/min and the optimal initial influent concentration of 24mg/L are used in this study. The pH values used are 5, 6, and 7. The experimental parameter is described in table 4 and the breakthrough point of each study is shown in Fig.-9.

According to the data shown that were no significant differences adsorption capacity between ffluent pH 5,6,7. The result showed that the highest amount of adsorption capacity was observed at pH 6. The adsorptive ability of an adsorbent is influence by the pH of adsorbate. This is because the protonation and deprotonation of the active site of the adsorbent³⁴. In the low pH surface acid conditions the adsorbent is also positively charged, cause a repulsion between the adsorbent surface and the metal ion, resulting in low adsorption. However at pH 7, The presence of OH ions in aqueous solution causes the interaction between Cd and OH- to result deposit cadmium hydroxide Cd(OH)₂ so that the adsorption capacity becomes decreased³⁴.

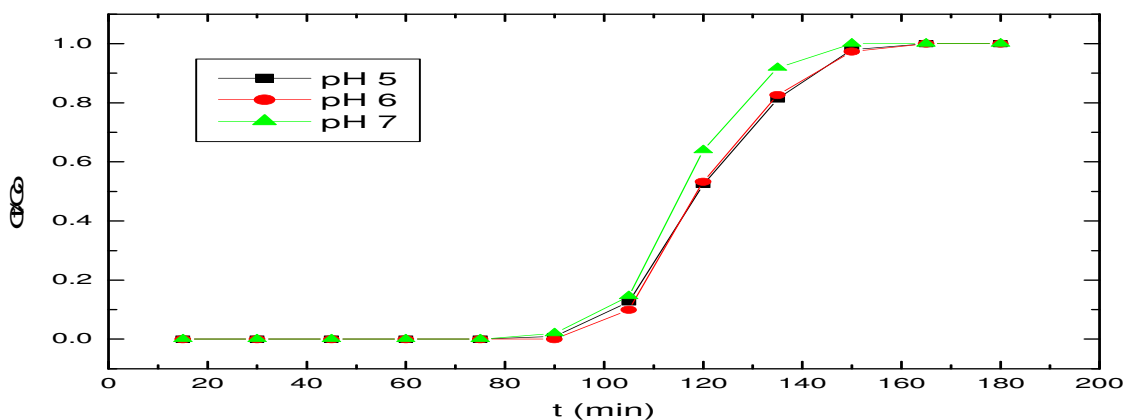


Fig.-9: Breakthrough Curves for Cadmium (II) Adsorption by Silica for Different pH 5,6,7

CONCLUSION

The silica gel is well synthesized by using volcanic ash base on Sinabung Mountain. The silica gel consists of -OH from Si-OH and Si-O from Si-O-Si. The silica gel is well generated on this research is amorphous, average pore radius of $1,5469 \times 10^{-1}$ Å, the surface area of silica gel is 374.994 m²/g which it is possible to be applied as an adsorbent. The optimum adsorption capacity of silica gel to metal ion of Cd (II) with fixed bed column method is: Flow rate 4mL / min with metal ion

adsorption capacity of Cd (II) equal to 21,194 mg / g. The initial optimum concentration was 24 ppm with an adsorption capacity of 21.632 mg / g. The optimum pH is pH 6, wherein the adsorption capacity of Cd (II) metal ions is 21.848 mg / g.

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